

# Metastability effects in strained and stressed SrTiO<sub>3</sub> films

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The sequence of ground states for SrTiO<sub>3</sub> film subjected to epitaxial strain as well as to mechanical stress along the [001] and [110] axes is calculated from first principles within the density functional theory. Under the fixed-strain boundary conditions, an increase in the lattice parameter of a substrate results in the  $I4cm \rightarrow I4/mcm \rightarrow Ima2 \rightarrow Cm \rightarrow Fmm2 \rightarrow Ima2(II)$  sequence of ground states. Under the fixed-stress boundary conditions, the phase sequence is different and depends on how the stress is applied. It is revealed that the simultaneous presence of competing ferroelectric and antiferrodistortive instabilities in SrTiO<sub>3</sub> gives rise to the appearance of metastable phases, whose number increases dramatically under the fixed-stress conditions. In the metastable phases, the octahedral rotation patterns are shown to differ substantially from those in the ground state. It is suggested that in systems with competing instabilities, each polar phase has its optimal octahedral rotation pattern which stabilizes this phase and creates a potential barrier preventing this phase to be transformed into other structures.

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## I. INTRODUCTION

Elastic strain is widely used today to improve the properties of electronic materials. For example, the effect of the strain-induced decrease of the acceptor binding energy in germanium enabled to create unique photodetectors working in the far infrared.<sup>1</sup> An increase of the electron mobility in strained silicon enabled to considerably improve the performance of silicon field-effect transistors,<sup>2</sup> and the use of highly strained layers in pseudomorphic high electron mobility transistors made it possible to deliberately tune the energy diagrams of these heterostructures in order to significantly improve their characteristics.<sup>3</sup>

The appearance of a strain-induced ferroelectricity in different dielectrics significantly extends the functionality of these materials and enables to offer new, previously known designs of electronic devices. The strain of incipient ferroelectrics leads to particularly impressive results.<sup>4–10</sup> For example, the stretching of thin films of strontium titanate SrTiO<sub>3</sub> grown on DyScO<sub>3</sub> substrates increases the Curie temperature in this material, which is nonpolar in the absence of strain, to  $\sim 300$  K,<sup>5</sup> and the compression of these films grown on silicon substrates increases this temperature up to  $\sim 410$  K (Ref. 9).

Strontium titanate is an incipient ferroelectric exhibiting a competition between the ferroelectric and antiferrodistortive (octahedral rotational) instabilities.<sup>11</sup> The latter of them is the cause of the phase transition observed in SrTiO<sub>3</sub> at about 105 K. The first work in which the influence of strain on the ferroelectric properties of strontium titanate was considered within the phenomenological approach was the work of Uwe and Sakudo.<sup>12</sup> Pertsev *et al.*<sup>4</sup> have developed this approach to describe the effect of the epitaxial strain on SrTiO<sub>3</sub> thin films. By expanding the thermodynamic potential in a power series of two order parameters (polarization and octahedral rotation) to the fourth order, the authors ob-

tained a rich pressure–temperature phase diagram with a large number of different phases. For the set of material constants of SrTiO<sub>3</sub> used by the authors, all obtained solutions had the order parameters directed along the axes of the cubic structure. Subsequent first-principles calculations in which the antiferrodistortive instability was neglected,<sup>13–15</sup> however, have shown that in stretched SrTiO<sub>3</sub> films the polarization should be directed along the [110] axis, in agreement with the experimental data.<sup>16,17</sup> A more thorough first-principles study of the low-temperature phases of SrTiO<sub>3</sub>, in which both ferroelectric and antiferrodistortive instabilities were taken into account,<sup>18</sup> showed that in highly stretched SrTiO<sub>3</sub> films the polarization is indeed directed along the [110] axis, but at low strain a phase with the [100] polarization appears. This orientation of the polarization was observed later in anisotropically strained SrTiO<sub>3</sub> films grown on GdScO<sub>3</sub> and DyScO<sub>3</sub> substrates.<sup>19,20</sup> The phase diagrams of strained SrTiO<sub>3</sub> for other sets of material constants were studied within the phenomenological and the phase-field approaches in Refs. 17, 21–23.

When studying the strain effects on the properties of different materials, the fixed-strain boundary conditions are usually used. However, the study of the fixed-stress boundary conditions is also important for real systems. To explain this, let's consider a thin epitaxial film which has domain structure and is fixed on a substrate. If the substrate is incompressible, then the in-plane lattice parameters in these domains would be equal to the lattice parameter of the substrate. However, in real systems the lattice parameters in the domains will be different because the substrate is compressible, and the difference between them will increase with increasing film thickness. In the limit of highly compressible (flexible) substrate, if one neglects mechanical and electrical boundary conditions at the domain walls, we come to the fixed-stress boundary conditions. In practice, the fixed-strain boundary conditions can be realized in ultrathin epitaxial films,

whereas the fixed biaxial stress boundary conditions can be realized in films grown on flexible substrates or thin plates which are fixed at their edges on a set of piezoelectric actuators. The actual boundary conditions in real systems are intermediate between the two limiting cases, and this is why the analysis of both cases is necessary when studying the strain effects.

In this work, we consider the ferroelectric and antiferrodistortive instabilities in  $\text{SrTiO}_3$  under the fixed-stress boundary conditions and compare them with the results obtained for the fixed-strain boundary conditions. Two different ways of applying stress to the film are examined: a uniaxial stress normal to the film plane and a biaxial stress in the film plane. We show that these two ways of applying stress result in different phase diagrams. We demonstrate that the simultaneous presence of competing ferroelectric and antiferrodistortive instabilities in  $\text{SrTiO}_3$  gives rise to the appearance of previously unknown metastable phases, whose number increases dramatically under the fixed-stress conditions, and explain the origin of the metastability.

## II. CALCULATION TECHNIQUE

Elastic deformation of  $\text{SrTiO}_3$  films was realized in two ways. To create the fixed-strain boundary conditions, the (001)-oriented film was grown on a cubic substrate with the lattice parameter  $a_0$ , which was varied within  $\pm 2\%$  of the lattice parameter of cubic strontium titanate. To create the fixed-stress boundary conditions, the stress was applied along the  $z$  axis normal to the film plane (the pressure is  $p_{[001]}$ ) or in the  $xy$  plane (the pressure is  $p_{[110]}$ ). The film was considered free to relax in directions normal to the applied stress or strain.

Calculations of the equilibrium lattice parameters and atomic positions in films were performed within the first-principles density functional theory using the ABINIT software. The exchange-correlation interaction was described in the local density approximation (LDA). The pseudopotentials of atoms constructed using the RKKJ scheme<sup>24</sup> were borrowed from Ref. 25. The plane-wave cutoff energy was 30 Ha (816 eV), the accuracy of self-consistent energy calculations was better than  $10^{-10}$  Ha. For the integration over the Brillouin zone, a  $8 \times 8 \times 8$  Monkhorst-Pack mesh for the cubic cell or meshes with equivalent density of  $k$ -points for low-symmetry phases were used. The relaxation of atomic positions and lattice parameters was performed until the forces acting on the atoms become less than  $2 \cdot 10^{-6}$  Ha/Bohr (0.1 meV/Å). Near the boundaries between the phases, the accuracy of the relaxation was increased to  $2 \cdot 10^{-7}$  Ha/Bohr.

As the energy difference between some phases in this work can be as small as 0.1 meV, the accuracy and convergence of calculations are very important issues. Insufficient  $k$ -point density, parallel shift of all atoms in the unit cell, and different sets of  $k$ -points for different structures are the main sources of errors. The convergence

studies have shown that an increase of the  $k$ -point density by a factor of three changes the energies of phases by no more than 0.02 meV. More important errors may result from a parallel shift of all atoms in the unit cell. The standard deviation of the energy of phases calculated for 20 different random parallel shifts was equal to 0.028 meV and was independent of the  $k$ -point density. As to the third source of errors, in most calculations we used the same sets of the  $k$ -points when performing the integration over the Brillouin zone, but the tests have shown that the changes in the energy of phases calculated for different sets of  $k$ -points do not exceed 0.03 meV. The errors in the enthalpy calculations resulting from variations of the unit cell volume and local stresses were less than 0.003 meV. So, the accuracy of our calculations enables to reliably distinguish the energy difference of 0.1 meV.

In searching for the ground state, after the relaxation of a structure of each relevant phase for each value of applied stress or strain, the phonon spectrum and the elastic tensor were calculated and it was checked whether all optical phonon frequencies at all high-symmetry points of the Brillouin zone are positive and whether the determinant and all leading principal minors constructed from components of the elastic tensor are positive (the stability criterion). If the criterion is not satisfied, small distortions corresponding to the least stable phonon were added to the structure, and the search for the ground state was continued. The technique of phonon spectra and elastic tensor calculations was similar to that described in Ref. 25. We considered only monodomain states because domain walls usually have a positive energy and so the multidomain solutions have a higher energy.

## III. RESULTS

The phonon spectrum calculations for the high-temperature  $Pm\bar{3}m$  phase of  $\text{SrTiO}_3$  confirmed a well-known result that there are three types of instabilities in the phonon spectrum: the ferroelectric one associated with the  $\Gamma_{15}$  mode at the center of the Brillouin zone and two antiferrodistortive instabilities with respect to rotations of the oxygen octahedra described by  $R_{25}$  and  $M_3$  modes at the boundary of the Brillouin zone.<sup>25,26</sup> Since the  $M_3$  instability is weak and disappears when the mode at the  $R$  point is condensed, we will neglect it when searching for the ground state. The calculations showed that in the absence of strain, the ground-state structure of strontium titanate is the  $I4/mcm$  phase.<sup>25</sup>

### A. Fixed-strain boundary conditions

To better understand the influence of the fixed-stress boundary conditions on the phase diagrams, we first consider the phase diagrams for  $\text{SrTiO}_3$  films grown on a cubic substrate (the fixed-strain boundary conditions).

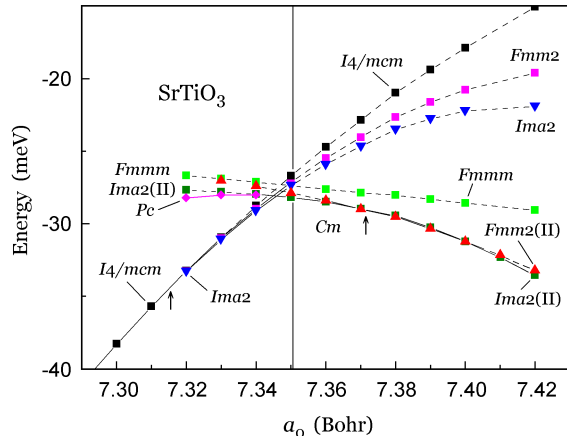


FIG. 1. (Color online) Energies of different phases for SrTiO<sub>3</sub> film grown on a cubic substrate with the lattice parameter  $a_0$ . The energy of high-symmetry  $P4/mmm$  phase is taken as the energy reference. The vertical line indicates the lattice parameter of cubic SrTiO<sub>3</sub>. Short arrows show the lattice parameters at which the frequencies of soft optical modes vanish.

Our calculations (Fig. 1) show that the sequence of the ground states [ $I4cm \rightarrow I4/mcm \rightarrow Imma2 \rightarrow Cm \rightarrow Fmmm2(II) \rightarrow Imma2(II)$ ] in this case is unexpectedly complex. The transition between the  $I4cm$  and  $I4/mcm$  phases occurs at  $a_0 \approx 7.279$  Bohr and is not shown in the figure (see Table A1 in the Appendix). At  $a_0 \approx 7.316$  Bohr, the  $I4/mcm$  phase becomes unstable and transforms to the  $Imma2$  phase, in which the octahedra are rotated around the  $[001]$  pseudocubic axis, whereas the polarization is along the  $[110]$  one (Table I). For all strains, this phase has a lower energy as compared to the  $Fmmm2$  phase in which the rotations are around the same axis, but the polarization is along the  $[100]$  axis. The transition between the  $Imma2$  and  $Cm$  phases occurs at  $a_0 \approx 7.345$  Bohr and is a first-order transition (the molar volumes of the two phases differ by 0.75% at the transition point). Near the phase transition point, the  $Cm$  phase can be regarded as a slightly distorted  $Imma2(II)$  phase,<sup>27</sup> but the polarization vector quickly rotates in the plane from the  $[110]$  to  $[100]$  direction with increasing  $a_0$ , and already at  $a_0 = 7.38$  Bohr the  $Fmmm2(II)$  phase becomes the ground state. At  $a_0 = 7.39$ – $7.40$  Bohr, the energy of the  $Fmmm2(II)$  phase turns out to be slightly lower than that of the  $Imma2(II)$  phase (by approximately 0.1 meV, see Table A1 in the Appendix for the energies of the phases). It is interesting that both phases with the lowest energy [ $Fmmm2(II)$  and  $Imma2(II)$ ] in this region satisfy the stability criterion (i.e., the former of them is stable and the latter is metastable), so that in this region the phases with polarizations along the  $[110]$  and  $[100]$  pseudocubic axes can coexist. This, in particular, enables to explain why two different orientations of polarization have been observed in two different experiments<sup>17,20</sup> on SrTiO<sub>3</sub> films grown on DyScO<sub>3</sub> substrates

TABLE I. Space groups and order parameters for phases considered in this work. The first three symbols in the order parameter denote Cartesian coordinates of the polarization vector and the last three symbols denote the rotations around the pseudocubic axes. The lattice parameters and atomic positions for typical representatives of the structures can be found in Tables A3 to A12 in the Appendix.

Space group	Order parameter
$I4/mcm$	(000 00 $\phi$ )
$I4cm$	(00 $p$ 00 $\phi$ )
$Fmmm2$	( $p00$ 00 $\phi$ ), (0 $p0$ 00 $\phi$ )
$Imma2$	( $pp0$ 00 $\phi$ )
$Fmmm$	(000 0 $\phi0$ ), (000 $\phi00$ )
$Fmmm2(II)$	( $p00$ 0 $\phi0$ ), (0 $p0$ $\phi00$ )
$Imma2(II)$	( $pp0$ $\phi\phi0$ )
$Cm$	( $p_1p_20$ $\phi_1\phi_20$ )
$Fmmm2(III)$	(00 $p$ 0 $\phi0$ ), (00 $p$ $\phi00$ )
$Pc$	( $p_1p_1p_3\phi_1\phi_1\phi_3$ )

and to understand the sensitivity of polarization to the anisotropic strain of the substrate. At  $a_0 > 7.40$  Bohr, the  $Imma2(II)$  phase becomes the ground state.

## B. Fixed-stress boundary conditions

Under the fixed-stress boundary conditions, the sequence of the ground states resulting from compression or stretching of the film is different for two ways of applying stress. This follows from the difference between the equations used to calculate the enthalpy. At  $p \parallel [001]$ , the enthalpy is calculated using the formula  $H = E_{\text{tot}} + p_{[001]}V\epsilon_3$ , where  $E_{\text{tot}}$  is the total energy,  $p_{[001]}$  is the pressure,  $V$  is the unit cell volume, and  $\epsilon_3$  is the strain tensor component (in Voigt notation) normal to the film. At  $p \parallel [110]$ , the enthalpy is  $H = E_{\text{tot}} + p_{[110]}V(\epsilon_1 + \epsilon_2)$ , where  $\epsilon_1$  and  $\epsilon_2$  are the strain tensor components in the film plane.

When the stress is applied, the symmetry of the high-temperature  $Pm\bar{3}m$  phase is lowered to tetragonal  $P4/mmm$  phase. As for the low-temperature  $I4/mcm$  phase, the formation of two structures differing by the direction of octahedral rotation axis is possible under stress. Because of a noticeable spontaneous strain accompanying the octahedral rotations in the unit cell, the resulting  $I4/mcm$  phase has a lower enthalpy for biaxially compressed films and the  $Fmmm$  phase has a lower enthalpy for biaxially stretched films (Fig. 2). In this work, a positive sign of the applied stress means the compression and a negative one means the tension. Since the compression of the film along the  $z$  axis results in its expansion in the  $xy$  plane, to facilitate the comparison of results for two ways of applying stress, we used two opposite directions of the horizontal axis in Fig. 2. The in-plane strain of the film at a maximum pressure

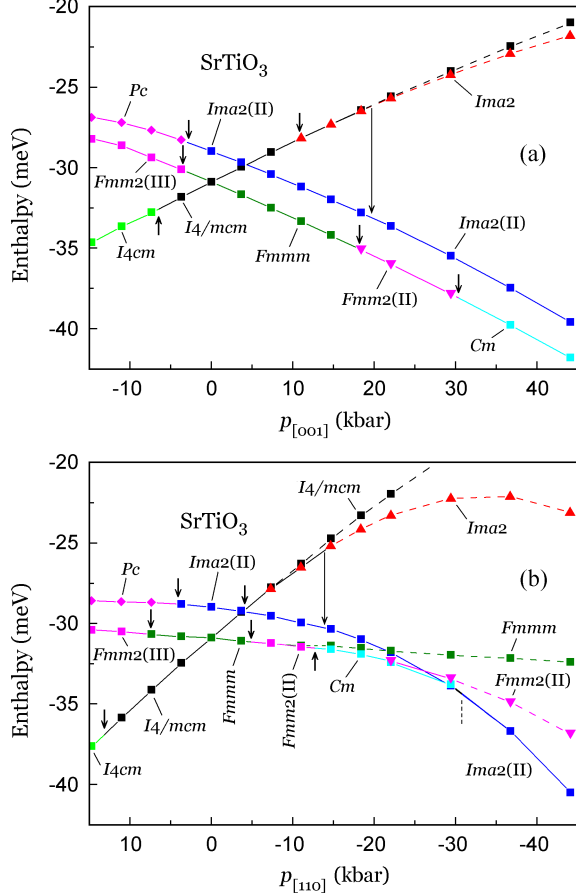


FIG. 2. (Color online) Enthalpies of different phases for SrTiO<sub>3</sub> film subjected to (a) uniaxial compression along the  $z$  axis and (b) biaxial stretching in the  $xy$  plane. The enthalpy of high-symmetry  $P4/mmm$  phase is taken as the energy reference. Short arrows indicate the stresses at which the frequencies of soft phonons vanish. Solid lines connecting the points refer to stable and metastable phases, whereas dashed lines indicate the unstable phases. Long vertical lines with arrows show the directions of structural relaxations at pressures where the metastable phases become unstable.

( $|p| = 44.1$  kbar) is 2.13% for  $p \parallel [001]$  and 1.85% for  $p \parallel [110]$ .

The existence region of the  $I4/mcm$  phase on the phase diagram depicted in Fig. 2 is limited by the softening of the ferroelectric  $A_{2u}$  mode (under the in-plane compression) and of the ferroelectric  $E_u$  mode (under the in-plane stretching). When crossing the boundaries of the existence region (shown by short vertical arrows in Fig. 2), the frequencies of corresponding modes become imaginary, and the symmetry of the unit cell is lowered, respectively, to  $I4cm$  and  $Ima2$ .<sup>28</sup> The same applies to the  $Fmmm$  phase, in which the softening of the  $B_{1u}$  mode upon the in-plane compression results in the appearance of the  $Fmm2(III)$  phase polarized along the  $z$  axis, and the softening of the  $B_{3u}$  mode upon the in-plane stretch-

ing results in the appearance of the  $Fmm2(II)$  phase polarized along the  $x$  axis (we assume that in both cases the octahedral rotations are around the  $y$  axis). We note that for two ways of applying stress we are discussing, the values at which the phase transitions occur are very different. For example, for the  $I4/mcm-I4cm$  phase transition the transition pressures are  $p_{[001]} = -6.5$  kbar and  $p_{[110]} = +13.1$  kbar.

While there is only one  $I4/mcm-I4cm$  phase transition in the in-plane compressed SrTiO<sub>3</sub> films, the sequence of the ground states in stretched films is much more complex. The calculations of the phonon spectra of the  $Fmmm$  phase show that with increasing in-plane stretching not only the polar  $B_{3u}$  mode is softened, but also the polar  $B_{2u}$  mode is softened. At a pressure of  $p_{[110]} = -4.9$  kbar or  $p_{[001]} = +18.2$  kbar, the former mode results in the transition to the  $Fmm2(II)$  phase polarized along the  $x$  axis. With further increase of pressure (at  $-12.7$  kbar or  $+30.3$  kbar, respectively), the  $B_{2u}$  mode induces the transition to the  $Cm$  phase, in which the polarization is rotated in the  $xy$  plane. For the in-plane stretching, the  $Cm$  phase transforms to the  $Ima2(II)$  phase at  $\sim 30$  kbar [see Fig 2(b) and enthalpies of different phases in Table A2 in the Appendix]. In the case of the out-of-plane compression, the  $Cm$  phase remains the ground state up to at least 45 kbar [Fig. 2(a)].

The pressure dependence of two components of spontaneous polarization for both ways of applying stress is shown in Fig. 3. The changes in polarization upon the  $Fmmm \rightarrow Fmm2(II)$  and  $Fmm2(II) \rightarrow Cm$  phase transitions and the fact that the polarization abruptly changes from the  $P_x \neq P_y$  state in the  $Cm$  phase to the  $P_x = P_y$  state characteristic of the  $Ima2(II)$  phase are clearly seen. From the comparison of the polarizations for two ways of applying stress it follows that the polarization is about 2.5 times higher for biaxial stretching than for uniaxial compression, whereas the phase sequence is the same. The reason for this is simple: the  $p_{[110]}V(\epsilon_1 + \epsilon_2)$  term in the enthalpy makes larger in-plane strains more favorable under  $p_{[110]} < 0$ . As the in-plane polarization strongly increases with increasing tensile strain ( $\epsilon_1 + \epsilon_2$ ), the polarization in biaxially stretched films is considerably higher than that in uniaxially compressed films. Under the  $p \parallel [001]$  compression, the polarization in  $Fmm2(II)$  and  $Cm$  phases is much lower than that in the metastable  $Ima2(II)$  phase because the rotation around the  $[100]$  axis strongly reduces the ( $\epsilon_1 + \epsilon_2$ ) values.

### C. Hysteresis and metastability effects

An analysis of the stress dependence of the soft-mode frequencies in the ground states of SrTiO<sub>3</sub> for the fixed-stress boundary conditions (Fig. 4) reveals a number of previously known features. First, the pressures, at which the extrapolated squares of the soft-mode frequencies vanish on both sides of the  $I4/mcm-I4cm$  phase tran-

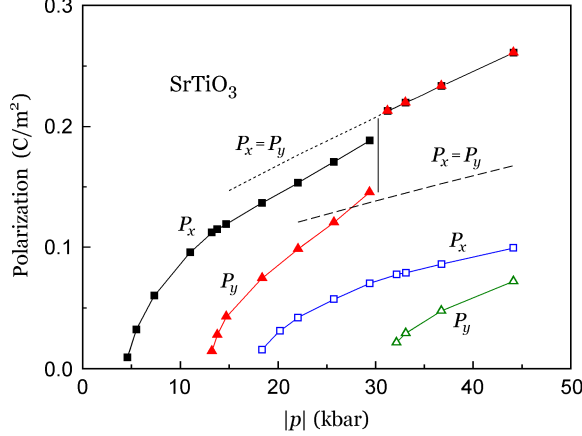


FIG. 3. (Color online) Components of polarization as a function of pressure for two ways of applying stress. Data for tensile  $p \parallel [110]$  stress are shown by filled symbols and data for compressive  $p \parallel [001]$  stress are shown by open symbols. The dotted and dashed lines show the polarization in the  $Ima2(II)$  phase obtained for  $p \parallel [110]$  and  $p \parallel [001]$ , respectively.

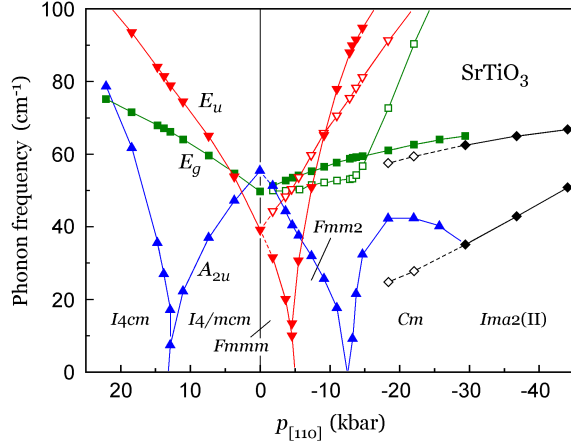


FIG. 4. (Color online) Frequencies of low-energy phonons in the ground-state structures as a function of the in-plane stress ( $p \parallel [110]$ ). Dotted lines show the behavior of frequencies in the metastable  $Ima2(II)$  phase that coexists with the ground-state  $Cm$  structure.

sition, differ by 0.76 kbar for  $p \parallel [110]$  (hysteresis loops are not shown in the figure). For  $p \parallel [001]$ , the difference between these pressures is more significant, 1.88 kbar. This means that in both cases the  $I4/mcm$ – $I4cm$  phase transition is of the first order. Similar phenomena are observed for the  $Fmmm$ – $Fmm2(II)$  phase transition (the hysteresis region width is 0.48 kbar for  $p \parallel [110]$  and 0.41 kbar for  $p \parallel [001]$ ) and for the  $Fmm2(II)$ – $Cm$  phase transition (the hysteresis region width is 0.39 kbar for  $p \parallel [110]$  and 0.62 kbar for  $p \parallel [001]$ ).

The most unusual phase transition in Fig. 4 is the  $Cm \rightarrow Imma2(II)$  one which is observed in biaxially

stretched films. As follows from Fig. 3, an abrupt change in polarization at this transition is an evidence of the first-order phase transition. This conclusion is consistent with the absence of any critical phonon mode softening on both sides of this transition (Fig. 4). Interestingly, that at pressures below the transition pressure, both structures [ $Cm$  and  $Ima2(II)$ ] satisfy the stability criterion, which means that the  $Ima2(II)$  phase with a higher enthalpy is *metastable* at these pressures. We attribute the transition under discussion to a “sliding off” of the structure, which occurs when the enthalpy of the  $Ima2(II)$  phase becomes lower than that of the  $Cm$  phase: thanks to the closeness of structures, the height of the potential barrier separating them is low.

It is interesting to also consider the chain of phase transitions occurring on a branch starting from the  $I4/mcm$  phase which is metastable at tensile stresses (Fig. 2).<sup>29</sup> The calculations of the phonon spectra for the  $I4/mcm$  phase show that not only the  $E_u$  mode is softened with increasing tensile stress, but also the  $E_g$  mode is softened, and after the phase transition to the  $Ima2$  phase at  $-4.1$  kbar it splits into two components (Fig. 5). At  $-13.8$  kbar, the frequency of one of its components vanishes. Adding of the distortions corresponding to this unstable mode to the  $Ima2$  structure causes its relaxation into a phase which has the same space group, but a different octahedral rotations pattern. This is already familiar to us the  $Ima2(II)$  phase, which was obtained earlier upon stretching the film along the  $I4/mcm \rightarrow Fmmm \rightarrow Fmm2(II) \rightarrow Cm \rightarrow Imma2(II)$  chain. As the  $E_g$  mode originates from the  $R_{25}$  mode of cubic  $SrTiO_3$ , the cause of the phase transition at  $-13.8$  kbar is the antiferrodistortive instability, which results in a change of the octahedral rotation axis direction from one normal to the film plane in the  $Ima2$  phase to one along the polar  $[110]$  pseudocubic axis in the  $Ima2(II)$  phase. It is unusual here that upon the relaxation, the  $Ima2$  structure transforms through an intermediate  $Cc$  phase into the *metastable*  $Ima2(II)$  phase, rather than into the ground-state structure [the  $Cm$  phase according to Fig. 2(b)].

Similar phenomena are observed in uniaxially stressed  $SrTiO_3$  films at  $p_{[001]} = +19.7$  kbar [Fig. 2(a)]. The  $Ima2$  structure, which becomes unstable above this pressure, also relaxes into the metastable  $Ima2(II)$  phase rather than into the ground-state structure [ $Fmm2(II)$  or  $Cm$ ].

The metastability effects are also characteristic of the  $Ima2(II)$  phase at  $p_{[001]} = 15$ – $37$  kbar and at  $p_{[110]} = -(11$ – $22)$  kbar (Fig. 3).

The behavior of the soft mode frequency in the  $Ima2(II)$  phase when changing the in-plane tensile stress is also interesting. As follows from Fig. 5, at the isostructural  $Ima2$ – $Ima2(II)$  phase transition, the majority of modes abruptly change their frequencies (dashed lines in the figure), whereas the frequency of the soft mode does not vanish when approaching to the phase boundary from the  $Ima2(II)$  phase. This means that this phase transition is of the first order. This conclusion



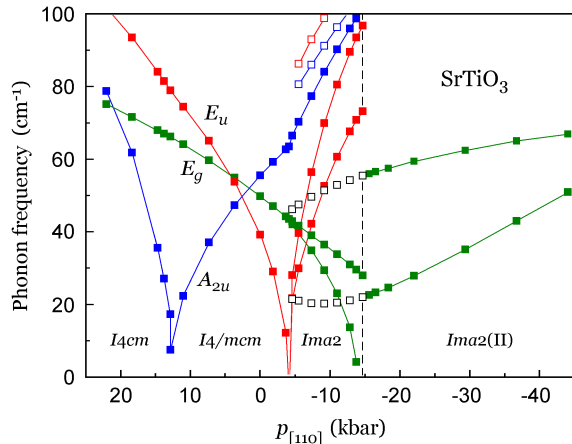


FIG. 5. (Color online) Frequencies of low-energy phonons in stable ( $I4cm$ ,  $I4/mcm$ ) and metastable [ $Ima2$ ,  $Ima2(II)$ ] phases as a function of  $p \parallel [110]$  stress. The frequencies in the  $Ima2(II)$  phase obtained upon releasing the in-plane stress are shown by open symbols.

is also confirmed by the ability to preserve the stability of the  $Ima2(II)$  phase when gradually decreasing tensile stress (open symbols in Fig. 5). Thus, in the pressure range from  $-4.1$  to  $-13.8$  kbar, a hysteresis region occurs on the considered branch of the phase diagram.<sup>30</sup> In this region, both  $Ima2$  and  $Ima2(II)$  phases satisfy the stability criterion, which means, if one takes into account the enthalpies of these phases [Fig. 2(b)], that both phases are metastable. The unusual property of the  $I4/mcm \rightarrow Ima2 \rightarrow Ima2(II)$  chain of transformations is that the phase transition at  $p_{[110]} = -4.1$  kbar occurs from a nonpolar to a *metastable* polar phase, which transforms into *another isostructural metastable* polar phase with increasing stress (at  $-13.8$  kbar).

The properties of polar phases coexisting in the hysteresis region differ significantly. At  $p_{[110]} = -11$  kbar, the values of spontaneous polarization are  $0.128$  C/m<sup>2</sup> in the  $Ima2$  phase,  $0.182$  C/m<sup>2</sup> in the  $Ima2(II)$  phase, and  $0.096$  C/m<sup>2</sup> in the ground-state  $Fmm2(II)$  phase. The band gaps calculated in the LDA approximation are  $1.795$  eV in the  $Fmm2(II)$  phase,  $1.825$  eV in the  $Ima2$  phase, and  $1.861$  eV in the  $Ima2(II)$  phase.

## IV. DISCUSSION

### A. Phase diagrams of strained and stressed SrTiO<sub>3</sub> films

#### 1. Strained SrTiO<sub>3</sub> films

To start, we compare the phase diagrams obtained in this work for SrTiO<sub>3</sub> film grown on a cubic substrate (the fixed-strain boundary conditions) with the results

of previous investigations.

At compressive strain, the results of this paper and previous works<sup>4,17,18</sup> are in good agreement and differ only in the strain values at which the  $I4/mcm$ – $I4cm$  phase transition occurs. This is not surprising if we take into account the difference in the sets of material constants used in phenomenological models and the difference in the calculation techniques and schemes of the pseudopotential construction used in first-principles calculations. The difference in the  $a_0$  values, at which the extrapolated squares of the soft-mode frequencies vanish at two sides of this phase transition, was found to be only  $0.00024$  Bohr in our calculations, which indicates that the transition is close to the second-order one.

At tensile strain, the results of our and previous calculations are much more different. In the phenomenological model,<sup>4</sup> in stretched films at all strains the polarization is directed along the  $\langle 100 \rangle$  pseudocubic axis, so that our solutions  $Ima2$ ,  $Ima2(II)$ , and  $Cm$  are absent. In the phenomenological model<sup>17</sup> it was shown that the  $Ima2$  and  $Ima2(II)$  solutions appear at low values of the  $\alpha_{12}$  coefficient for the  $(P_x^2 P_y^2 + P_x^2 P_z^2 + P_y^2 P_z^2)$  term, and the  $Ima2$  phase is stable only in a narrow region of negative strains. Both these phases disappear with increasing  $\alpha_{12}$  (the solution obtained in this case agrees with that of Ref. 4), and the  $Cm$  phase does not appear at all. The optimal value of the  $\alpha_{12}$  coefficient for which the predictions of the phenomenological model are closest to the experiment was found in Ref. 22. In the phase-field model<sup>23</sup> at  $T \rightarrow 0$  the  $Ima2$  phase is absent, and it is not clear whether the  $Cm$  solution at high strains can be associated with our  $Ima2(II)$  phase. Our results also differ from those of the phenomenological model,<sup>21</sup> in which its own set of material constants was used. According to Ref. 21, when the lattice parameter  $a_0$  is increased, the ground-state structures change as follows:  $P4mm \rightarrow I4cm \rightarrow I4/mcm \rightarrow Ima2 \rightarrow Fmm2(II) \rightarrow Cm \rightarrow Ima2(II) \rightarrow Amm2$ , whereas our calculations predict the sequence  $I4cm \rightarrow I4/mcm \rightarrow Ima2 \rightarrow Cm \rightarrow Fmm2(II) \rightarrow Ima2(II)$  and that the  $P4mm$  and  $Amm2$  phases never become the ground-state structures. As for the comparison with the results of first-principles calculations that took into account both order parameters,<sup>18</sup> in the cited work the existence regions of the  $Ima2$  and  $Ima2(II)$  phases are separated by an intermediate  $Fmm2(II)$  phase. In our calculations, the sequence of the ground-state structures for stretched films differs from the data of Ref. 18 in that the transition between the  $Ima2$  and  $Cm$  phases occurs abruptly, and the  $Fmm2(II)$  phase is the ground-state structure only in a narrow region separating the  $Cm$  and  $Ima2(II)$  phases (Fig. 1).

#### 2. Stressed SrTiO<sub>3</sub> films

We now consider the differences between the phase diagrams obtained under the fixed-stress boundary condi-

tions for two ways of applying stress and the phase diagrams obtained above under the fixed-strain conditions.

In biaxially compressed film ( $p \parallel [110]$ ), the transition pressures of the  $I4cm-I4/mcm$  and  $I4/mcm-Ima2$  phase transitions are close to the values of internal stress at the transition points in films grown on a cubic substrate (with a maximum deviation of 0.3–0.6 kbar). In contrast, at the biaxial stretching, the phase diagrams differ much stronger [compare Fig. 1 and Fig. 2(b)]. This is because under tension, the  $Fmm2(II)$ ,  $Cm$ , and  $Ima2(II)$  phases (in which spontaneous strains caused by polarization and octahedral rotations lie in the film plane) become energetically more favorable. At low stresses, a configuration in which the two components of spontaneous strain are perpendicular to each other is the most favorable, and at high stresses, a configuration in which the spontaneous strains are parallel to each other and are directed along the  $[110]$  pseudocubic axis is the most favorable. Due to an additional contribution to the enthalpy proportional to  $\epsilon_1 + \epsilon_2 = -p_{[110]}S^{(2D)}$  (where a “two-dimensional” elastic compliance  $S^{(2D)}$  is the sum of  $S_{11} + S_{22} + 2S_{12}$  elastic compliance tensor components in Voigt notation), the phase with the highest  $S^{(2D)}$  is characterized by the strongest decrease of the enthalpy with increasing stress, and so it is asymptotically the most stable. In our case, this is the  $Ima2(II)$  phase.

Under uniaxial tension ( $p \parallel [001]$ ), the phases in which the spontaneous strain is directed along the  $z$  axis (under tension) or those in which the spontaneous strain lies in the film plane (under compression) should be more energetically favorable. However, we should note that the condition for the occurrence of a phase transition under uniaxial stress differ significantly from the condition for the case of biaxial stress. For example, the lattice parameter  $a_0$  at which the  $I4/mcm-I4cm$  phase transition occurs in  $SrTiO_3$  is 7.2785 Bohr for  $p \parallel [110]$  and 7.3018 Bohr for  $p \parallel [001]$ . This reduces the transition pressure into the  $I4cm$  phase and strongly increases the transition pressures into the  $Fmm2(II)$  and  $Cm$  phases. As an additional contribution to the enthalpy for  $p \parallel [001]$  is proportional to  $\epsilon_3 = -p_{[001]}S_{33}$ , in this case asymptotically the most stable phase is that with the highest  $S_{33}$  value. This phase is also the  $Ima2(II)$  phase, but because the transition pressure into this phase under uniaxial compression is sufficiently high ( $\sim 85$  kbar), this phase does not become the ground state in the pressure range considered in this work [Fig. 2(a)].

As we have seen, the transition from the fixed-strain to the fixed-stress boundary conditions causes a change in the order of phase transitions: they become the first-order ones, and the width of the corresponding hysteresis regions depend on the way of applying stress. We attribute the change in the order of phase transitions to a well-known renormalization of the coefficients of the fourth-order terms in the Landau expansion produced by electrostriction, which results in that the second-order phase transitions can become the first-order ones. The fact that the lattice parameters (as well as the atomic

positions) near the phase transition points are significantly different for two ways of applying stress enables to explain why the width of the hysteresis regions near these points depends on how the stress is applied. It is important to note that the mere fact of appearance of the first-order phase transitions in  $SrTiO_3$  means that the phenomenological description of its properties should take into account at least the sixth-order terms in the power series expansion of the thermodynamic potential.

## B. The nature of metastability effects

The most interesting result of this work is the observation of metastable phases and phase transitions between them in strained and stressed  $SrTiO_3$  films. We believe that the appearance of these phenomena is due to competing instabilities in this material.

Indeed, these phenomena were absent in the first-principles calculations in which the octahedral rotations were neglected.<sup>13–15</sup> These calculations predicted the second-order  $P4/mmm \rightarrow P4mm$  phase transition in biaxially compressed films and the second-order  $P4/mmm \rightarrow Amm2$  one in biaxially tensile films. According to our calculations, in which octahedral rotations were neglected, at  $p = 0$  the most stable phase is  $R3m$ ,<sup>25</sup> and the biaxial strain transforms it via an intermediate  $Cm$  phase, respectively, to the  $P4mm$  phase (at  $a_0 \approx 7.341$  Bohr) or to the  $Amm2$  phase (at  $a_0 \approx 7.361$  Bohr).<sup>31</sup> No signs of metastability were observed in these calculations.

When both ferroelectric and antiferrodistortive instabilities in  $SrTiO_3$  are taken into account, the metastability appears already under the fixed-strain boundary conditions. It is observed in the  $Fmm2(II)$  and  $Ima2(II)$  phases at  $a_0 = 7.39$ –7.40 Bohr and in the  $Pc$  phase, to which an unstable  $Ima2(II)$  phase relaxes at  $a_0 = 7.32$ –7.34 Bohr upon condensation of two unstable phonons at the center and at the boundary of the Brillouin zone (the energy of the  $Pc$  phase is significantly higher than that of the ground-state  $I4/mcm$  or  $Ima2$  phases, Fig. 1). The signs of metastability can also be observed in the region  $a_0 = 7.35$ –7.37 Bohr where *two different solutions* with the  $Cm$  symmetry and different orientation of the polarization, which both satisfy the stability criterion, appear as a result of relaxation of unstable  $Ima2(II)$  and  $Fmm2(II)$  phases.

A particularly large number of metastable phases appears in  $SrTiO_3$  under the fixed-stress boundary conditions. Under these conditions, the majority of phases, which were simply unstable under fixed-strain conditions, become metastable (in Fig. 2 the points corresponding to these phases are connected by solid lines). An analysis shows that the octahedral rotation patterns in metastable phases are strongly different from those in the ground states. For example, for the  $Ima2$  phase, which is metastable under tensile stress, the transition to the ground state requires to change the direction of

the octahedral rotation axis from  $[001]$  to  $[110]$ , and for the  $Pc$  and  $Fmmm$  phases, which are metastable under compressive stress, the transition requires to change the direction from  $[11x]$  to  $[001]$  and from  $[010]$  to  $[001]$ , respectively. This suggests that each polar phase has its optimal octahedral rotation pattern which stabilizes this phase and creates a potential barrier preventing this phase to be easily transformed into another structure. Such a transformation needs to simultaneously shift a large number of the oxygen atoms involved in the octahedral rotations and to change the lattice parameters, so that the appearance of metastability is closely related to the antiferrodistortive instability. The height of the potential barrier separating the  $Ima2$  and  $Ima2(II)$  phases (which can be transformed into each other via an intermediate  $Amm2$  phase) is  $\sim 24$  meV per formula unit at  $p_{[110]} = -11$  kbar. The weakening of the metastability effects in films grown on cubic substrates, in which spontaneous strain cannot be fully realized, confirms this explanation. Nevertheless, the competition of the local distortions accompanying the appearance of polarization and octahedral rotations can be observed even in epitaxial films.

It should be noted that the metastability effects revealed in  $\text{SrTiO}_3$  films are qualitatively different from the effects typical for first-order phase transitions. In the latter case, the metastability appears in the hysteresis region where two phases described by different values of the same order parameter fulfill the stability criterion and so can coexist. In  $\text{SrTiO}_3$ , the metastability effects are due to a complex interaction between the polarization and the rotational order parameter via a striction mechanism. This explains why the obtained solutions turn out to be very sensitive to the mechanical boundary conditions.

The consequence of the metastability effects in systems with competing instabilities is the impossibility, in certain situations, to establish whether the obtained solution is the ground-state structure of a system, or just a metastable state. As shown in this work, the approach used in most first-principles investigations of phase transitions (according to which the ground state is searched by a successive approaching to the structure that satisfies the stability criterion) often results only in the metastable states. The ground state in these systems can be found only after exploring the entire phase diagram and all transitions between the phases. This analysis, however, can be facilitated by studying the phase diagrams under the fixed-strain boundary conditions.

It can be seen that the existence of metastable phenomena in  $\text{SrTiO}_3$  results in the appearance of bistability regions on the phase diagrams, in which stable and one or more metastable polar phases coexist. Let us discuss one interesting possibility of using this bistability. The phase sequence obtained on the  $I4cm-I4/mcm-Ima2$  branch in stretched  $\text{SrTiO}_3$  films [Fig. 2(b)] enables to offer one more possible application of such films in non-volatile phase change memory devices. Indeed, by applying a

specific sequence of stresses when cooling the film, a homogeneous metastable state in the hysteresis region (the  $Ima2$  phase) can be prepared in it. Then, the regions of equilibrium  $[Fmm2(II), Cm]$  or the other metastable  $[Ima2(II)]$  phases can be formed on the film surface by the local optical heating. Due to the bistability of the system, both phases can coexist at low temperatures for a long enough time, and a contrast in their optical properties can be used for nondestructive read-out of recorded information. Erasing of information can be easily realized by heating the film at zero stress.

The sequences of the ground states in  $\text{SrTiO}_3$  films obtained in this work as a function of applied strain and stress correspond to the case of  $T \rightarrow 0$ . At higher temperatures, the phase diagrams may become more complex because of the appearance of domain-like structures. Such a structure, which consisted of thick  $90^\circ$  domain walls, was revealed in a first-principles-based effective Hamiltonian molecular dynamics study of  $\text{BaTiO}_3$  films subjected to tensile strain in a wide temperature range below the Curie temperature.<sup>32</sup> In unstrained  $\text{BaTiO}_3$ , the existence region of this multidomain state coincided with that of the orthorhombic phase in bulk  $\text{BaTiO}_3$ . However, it remains unclear whether this multidomain structure is a real (static) one or just a correlated thermal motion of atoms because the presented data were averaged over a very short (4 ps) time interval. The existence of competing instabilities in  $\text{SrTiO}_3$  can complicate its domain structure. Its complex dynamic behavior and the metastability effects revealed in this work can result in enhanced loss tangent usually observed in ferroelectric phases because they both exhibit a retarded reaction to an applied electric field.

## V. CONCLUSIONS

The first-principles calculations of the phase diagrams of strained and stressed  $\text{SrTiO}_3$  films have revealed a number of previously unknown metastability effects which manifest themselves as coexistence of several phases all satisfying the stability criterion. These effects become particularly noticeable under the fixed-stress boundary conditions. It was shown that the cause of these effects is the existence of competing instabilities in this material. This suggests that similar phenomena may occur in other ferroelectrics with competing instabilities such as  $\text{NaNbO}_3$  and  $\text{BiFeO}_3$ .

The metastability effects are also important for understanding the phenomenon of antiferroelectricity because competing instabilities are very typical for antiferroelectric materials such as  $\text{PbZrO}_3$ . In particular, the electric-field-induced polar  $R3c$  phase in  $\text{PbZrO}_3$  is in fact a metastable phase, in which the octahedral rotation pattern differs from that in the ground-state nonpolar  $P6mm$  structure.

As for the results specific for  $\text{SrTiO}_3$ , it is clear that the phenomenological description of its properties



needs to take into account the higher-order terms in the Landau expansion, and so the results of previous studies within this approach require a further examination.

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## **Appendix: Supplemental material**

The energies and enthalpies of different phases calculated for a given strain or stress are compared in Tables A1 and A2. The optimized lattice parameters and atomic positions for all structures considered in this work are given in Tables A3 to A12.

TABLE A1. Energies of different phases in strained SrTiO<sub>3</sub> film fixed on a square substrate with a lattice parameter  $a_0$  (in meV). The energy of high-symmetry  $P4/mmm$  phase is taken as the energy reference. The energies of stable phases are in boldface.

$a_0$ (Bohr)	Phases							
	$I4/mcm$	$I4cm$	$Fmmm$	$Ima2$	$Fmm2$	$Ima2(II)$	$Fmm2(II)$	$Cm$
7.16	-93.03	<b>-95.72</b>	—	—	—	—	—	—
7.20	-73.46	<b>-74.53</b>	—	—	—	—	—	—
7.22	-64.97	<b>-65.53</b>	—	—	—	—	—	—
7.24	-57.19	<b>-57.47</b>	—	—	—	—	—	—
7.26	-50.17	<b>-50.28</b>	—	—	—	—	—	—
7.27	-46.95	<b>-46.97</b>	—	—	—	—	—	—
7.275	-45.40	<b>-45.43</b>	—	—	—	—	—	—
7.28	<b>-43.91</b>	—	—	—	—	—	—	—
7.29	<b>-41.01</b>	—	—	—	—	—	—	—
7.30	<b>-38.28</b>	—	—	—	—	—	—	—
7.31	<b>-35.70</b>	—	—	—	—	—	—	—
7.315	<b>-34.45</b>	—	—	—	—	—	—	—
7.32	-33.24	—	-26.67	<b>-33.26</b>	-33.23	-27.67	—	-28.21
7.33	-30.94	—	-26.89	<b>-31.07</b>	-30.99	-27.81	—	-28.03
7.34	-28.76	—	-27.12	<b>-29.09</b>	-28.96	-27.96	-27.40	-28.00
7.345	-27.71	—	-27.24	<b>-28.19</b>	-28.01	-28.03	-27.63	-28.05
7.35	-26.69	—	-27.36	-27.37	-27.12	<b>-28.17</b>	-27.87	<b>-28.17</b>
7.36	-24.71	—	-27.61	-25.89	-25.47	-28.48	-28.39	<b>-28.49</b>
7.37	-22.86	—	-27.86	-24.65	-24.04	-28.97	-28.99	<b>-29.04</b>
7.38	-20.98	—	-28.02	-23.49	-22.65	-29.44	-29.51	<b>-29.54</b>
7.39	-19.38	—	-28.30	-22.77	-21.62	-30.25	<b>-30.33</b>	—
7.40	-17.87	—	-28.58	-22.22	-20.77	-31.21	<b>-31.21</b>	—
7.42	-15.05	—	-29.07	-21.91	-19.61	<b>-33.55</b>	-33.19	—
7.44	-12.59	—	-29.56	-22.53	-19.29	<b>-36.65</b>	-35.56	—

TABLE A2. Entalpies of different phases in [110]-stressed SrTiO<sub>3</sub> film (in meV). The energy of high-symmetry  $P4/mmm$  phase is taken as the energy reference. The enthalpies of stable phases are in boldface.

$P_{[110]}$ (kbar)	Phases							
	$I4cm$	$I4/mcm$	$Ima2$	$Ima2(II)$	$Imma$	$Fmmm$	$Fmm2(II)$	$Cm$
44.13	—	—	-23.08	<b>-40.48</b>	—	-32.40	-36.86	—
36.78	—	—	-22.09	<b>-36.67</b>	—	-32.15	-34.88	—
29.42	—	-19.36	-22.21	<b>-33.86</b>	—	-31.96	-33.42	-33.80
22.07	—	-21.95	-23.26	-31.79	—	-31.70	-32.33	<b>-32.41</b>
18.39	—	-23.28	-24.11	-30.98	—	-31.53	-31.90	<b>-31.91</b>
14.71	—	-24.72	-25.15	-30.34	—	-31.39	<b>-31.55<sup>a</sup></b>	-31.54
11.03	—	-26.30	-26.48	-29.95	—	-31.39	<b>-31.45</b>	—
7.36	—	-27.76	-27.81	-29.53	-29.11	-31.21	<b>-31.24</b>	—
5.52	—	-28.52	-28.54	-29.37	-29.07	-31.10	<b>-31.12</b>	—
4.60	—	-28.91	-28.91	-29.28	-29.05	-31.06	<b>-31.08</b>	—
3.68	—	-29.30	—	-29.22	-29.02	<b>-31.02</b>	—	—
0.0	—	<b>-30.88</b>	—	-28.97	-28.92	-30.88	—	—
-3.68	—	<b>-32.45</b>	—	-28.80	—	-30.81	—	—
-7.36	—	<b>-34.12</b>	—	-28.70	—	-30.67	—	—
-11.03	—	<b>-35.86</b>	—	-28.59	—	-30.47	—	—
-14.71	<b>-37.69</b>	-37.63	—	-28.50	—	-30.35	—	—

<sup>a</sup> Response function calculations indicate an instability of this phase against its transformation into the  $Cm$  phase.

TABLE A3. Lattice parameters, Wyckoff positions, and atomic coordinates for the  $I4/mcm$  phase of  $\text{SrTiO}_3$  at  $p = 0$  (the rotations are around the  $[001]$  pseudocubic axis).

$a = 10.333105 \text{ Bohr}, c = 14.803747 \text{ Bohr}$				
Atom	WP	$x$	$y$	$z$
Sr	$4b$	0.000000	0.500000	0.250000
Ti	$4c$	0.000000	0.000000	0.000000
O	$4a$	0.000000	0.000000	0.250000
O	$8h$	0.214346	0.714346	0.000000

TABLE A4. Lattice parameters, Wyckoff positions, and atomic coordinates for the  $I4cm$  phase of  $\text{SrTiO}_3$  film fixed on a substrate with  $a_0 = 7.20 \text{ Bohr}$  (the rotations are around the  $[001]$  pseudocubic axis, the polarization is along the same axis).

$a = 10.182338 \text{ Bohr}, c = 14.996956 \text{ Bohr}$				
Atom	WP	$x$	$y$	$z$
Sr	$4b$	0.500000	0.000000	0.253951
Ti	$4a$	0.000000	0.000000	0.008361
O	$4a$	0.000000	0.000000	0.249368
O	$8c$	0.207733	0.707733	-0.000840

TABLE A5. Lattice parameters, Wyckoff positions, and atomic coordinates for the  $Fmmm$  phase of  $\text{SrTiO}_3$  film fixed on a substrate with  $a_0 = 7.38 \text{ Bohr}$  (the rotations are around the  $[010]$  axis).

$a = 14.760000 \text{ Bohr}, c = 14.593072 \text{ Bohr}$				
Atom	WP	$x$	$y$	$z$
Sr	$8h$	0.000000	0.250507	0.000000
Ti	$8d$	0.250000	0.000000	0.250000
O	$8i$	0.000000	0.000000	0.216530
O	$8f$	0.250000	0.250000	0.250000
O	$8g$	0.283971	0.000000	0.000000

TABLE A6. Lattice parameters, Wyckoff positions, and atomic coordinates for the  $Fmm2$  phase of  $\text{SrTiO}_3$  film fixed on a substrate with  $a_0 = 7.38 \text{ Bohr}$  (the polarization is along the  $[100]$  pseudocubic axis, the rotations are around the  $[001]$  axis; the  $F2mm$  setting).

$a = 14.760000 \text{ Bohr}, c = 14.703578 \text{ Bohr}$				
Atom	WP	$x$	$y$	$z$
Sr	$8d$	0.006484	0.000000	0.249962
Ti	$8c$	0.258024	0.249145	0.000000
O	$8c$	-0.000988	0.281480	0.000000
O	$4a$	0.218214	0.000000	0.000000
O	$4a$	-0.219248	0.000000	0.000000
O	$8b$	0.246996	0.250000	0.250000

TABLE A7. Lattice parameters, Wyckoff positions, and atomic coordinates for the  $Fmm2(\text{II})$  phase of  $\text{SrTiO}_3$  film fixed on a substrate with  $a_0 = 7.38 \text{ Bohr}$  (the polarization is along the  $[100]$  pseudocubic axis, the rotations are around the  $[010]$  axis; the  $F2mm$  setting).

$a = 14.760000 \text{ Bohr}, c = 14.591528 \text{ Bohr}$				
Atom	WP	$x$	$y$	$z$
Sr	$8c$	0.006027	0.250548	0.000000
Ti	$8d$	0.258045	0.000000	0.250988
O	$8d$	0.499078	0.000000	0.283937
O	$8b$	0.247904	0.250000	0.250000
O	$4a$	0.283166	0.000000	0.000000
O	$4a$	-0.285274	0.000000	0.000000

TABLE A8. Lattice parameters, Wyckoff positions, and atomic coordinates for the  $Ima2$  phase of  $\text{SrTiO}_3$  film fixed on a substrate with  $a_0 = 7.38 \text{ Bohr}$  (the polarization is along the  $[110]$  pseudocubic axis, the rotations are around the  $[001]$  axis; the  $I2am$  setting).

$a = 10.436896 \text{ Bohr}, c = 14.702085 \text{ Bohr}$				
Atom	WP	$x$	$y$	$z$
Sr	$4a$	0.511582	0.000000	0.000000
Ti	$4b$	0.014611	0.001526	0.250000
O	$4a$	-0.004529	0.000000	0.000000
O	$4b$	0.717532	0.218809	0.250000
O	$4b$	-0.219196	0.717984	0.250000

TABLE A9. Lattice parameters, Wyckoff positions, and atomic coordinates for the  $Ima2(\text{II})$  phase of  $\text{SrTiO}_3$  film fixed on a substrate with  $a_0 = 7.38 \text{ Bohr}$  (the polarization is along the  $[110]$  pseudocubic axis, the rotations are around the same axis; the  $I2am$  setting).

$a = 10.436896 \text{ Bohr}, c = 14.594969 \text{ Bohr}$				
Atom	WP	$x$	$y$	$z$
Sr	$4b$	0.510431	0.001862	0.250000
Ti	$4a$	0.012530	0.000000	0.000000
O	$4b$	0.497252	0.547074	0.250000
O	$8c$	0.250394	0.249830	0.024560

TABLE A10. Lattice parameters, Wyckoff positions, and atomic coordinates for the  $Cm$  phase of  $\text{SrTiO}_3$  film fixed on a substrate with  $a_0 = 7.36$  Bohr (the polarization and the rotation axis are in the  $xy$  plane; the  $Am$  setting).

$a = 10.408612$ Bohr, $c = 14.619606$ Bohr <sup>a</sup>				
Atom	WP	$x$	$y$	$z$
Sr	$2a$	0.504500	0.503322	0.000000
Sr	$2a$	0.505691	-0.000127	0.000000
Ti	$4b$	0.005456	0.002834	0.250500
O	$2a$	0.029421	0.454223	0.000000
O	$2a$	-0.029241	0.043574	0.000000
O	$4b$	0.001801	0.248585	0.280345
O	$4b$	0.501557	0.248085	0.734216

<sup>a</sup> The translation vectors are  $[100]$ ,  $[110]$ , and  $[001]$ .

TABLE A11. Lattice parameters, Wyckoff positions, and atomic coordinates for the  $Fmm2(\text{III})$  phase of  $\text{SrTiO}_3$  film subjected to a stress of  $p_{[001]} = -14.7$  kbar (the polarization is along the  $[001]$  pseudocubic axis, the rotations are around the  $[010]$  axis).

$a = 14.59641$ Bohr, $b = 14.77120$ Bohr, $c = 14.72473$ Bohr				
Atom	WP	$x$	$y$	$z$
Sr	$8c$	0.000000	0.249575	0.001152
Ti	$8d$	0.249152	0.000000	0.252941
O	$4a$	0.000000	0.000000	0.210624
O	$4a$	0.000000	0.000000	0.279767
O	$8b$	0.250000	0.250000	0.244342
O	$8d$	0.284337	0.000000	-0.004654

TABLE A12. Lattice parameters, Wyckoff positions, and atomic coordinates for the  $Pc$  phase of  $[001]$ -stressed  $\text{SrTiO}_3$  film ( $p_{[001]} = -14.7$  kbar); the  $Pa$  setting.

$a = 10.351368$ Bohr, $b = 10.405403$ Bohr, $c = 14.747770$ Bohr, $\beta = 89.9952^\circ$				
Atom	WP	$x$	$y$	$z$
Sr	$2a$	0.507791	0.252513	0.255092
Sr	$2a$	0.497563	0.247451	0.755063
Ti	$2a$	0.002976	0.248822	0.007148
Ti	$2a$	0.002331	0.251203	0.507150
O	$2a$	0.001328	0.204662	0.249255
O	$2a$	0.004428	0.295355	0.749257
O	$2a$	0.244962	-0.007996	-0.024935
O	$2a$	0.760337	0.507554	0.475052
O	$2a$	-0.738300	0.491565	0.022296
O	$2a$	-0.255419	0.007896	0.522307

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  - <sup>27</sup> This is proven by an instability of the phonon spectra of *Ima2*(II) and *Fmm2*(II) phases at  $a_0 = 7.35\text{--}7.37$  Bohr. For example, in the *Ima2*(II) phase, the eigenvector of unstable  $B_1$  phonon at the  $\Gamma$  point at  $a_0 = 7.36\text{--}7.37$  Bohr includes, in addition to polar displacements, the octahedral rotations around the  $y$  axis perpendicular to the polarization, whereas at  $a_0 = 7.35$  Bohr, the unstable phonon is at the boundary of the Brillouin zone and describes the *in-phase* octahedral rotations around the  $z$  axis (similar to those described by the  $M_3$  phonon in the cubic phase). The frequencies of these phonons are  $\sim 10i\text{ cm}^{-1}$ .
  - <sup>28</sup> Since the  $E_u$  mode is doubly degenerate, to find the ground state resulting from the ferroelectric instability of the *I4/mcm* phase we have to consider two structures described by two-component  $(P, 0)$  and  $(P, P)$  order parameters and to choose among them the structure with a lower enthalpy. Of the two possible solutions with space groups *Fmm2* and *Ima2*, the *Ima2* phase had a lower enthalpy.
  - <sup>29</sup> In principle, these phases can be prepared by cooling the film under compressive stress and after then by changing the sign of stress.
  - <sup>30</sup> The stability of the metastable *Ima2*(II) phase is retained up to a pressure of +4.1 kbar, above which it transforms to the *Pc* phase.
  - <sup>31</sup> The appearance of a gap between the *P4mm* and *Amm2* polar phases is typical of calculations in which the theoretical lattice parameter of cubic  $\text{SrTiO}_3$  was  $a_0 = 7.27\text{--}7.285$  Bohr.<sup>13–15</sup> In Ref. 33, where  $a_0 = 7.303$  Bohr, the lowest-energy phase at  $p = 0$  was already the *R3m* phase. The pseudopotentials and calculation technique used in this work give a value of  $a_0 = 7.3506$  Bohr, which is closest to the experiment ( $a_0 = 7.379$  Bohr at 300 K). This effect is obviously associated with an effective pressure that exists in all LDA calculations (with underestimated lattice parameter) and influences the ferroelectric instability.
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